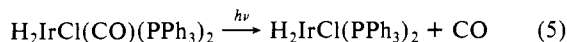
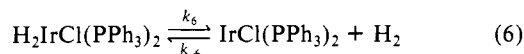


$(2.6 \pm 0.7) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ within experimental uncertainty of the k_{co} reported for eq 3.

These results indicate that $\text{H}_2\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ first undergoes photodissociation of CO (eq 5) followed by elimination of H_2 from



the resulting pentacoordinated intermediate (eq 6) to give the



" $\text{IrCl}(\text{PPh}_3)_2$ " transient formed directly via flash photolysis of *trans*- $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$. This view⁸ contrasts to the proposal⁹ that the dihydride photoelimination occurs by a single concerted step but is consistent with theoretical arguments⁴ and several experimental observations^{10,11} that reductive elimination from d^6 complexes often occurs much more readily after ligand dissociation from the original hexacoordinate species to give a pentacoordinate intermediate. Given that formation of $\text{IrCl}(\text{PPh}_3)_2$ was complete within the lifetime of the flash (20 μs), a lower limit for k_6 can be estimated as $5 \times 10^4 \text{ s}^{-1}$. Thus, we conclude that dissociation of CO accelerates dihydrogen elimination by at least 9 orders of magnitude. Notably, this rate acceleration occurs despite the dissociation of the π -acid CO which would be expected to favor the lower oxidation state of the metal center. Another notable feature is that the equilibrium indicated by eq 6 apparently lies largely to the right in contrast to the observation that under similar conditions the equilibrium for the Rh(I) analogue must lie to the left.⁷

Preliminary investigations of the Ir(III) species $\text{H}^+\text{IrCl}(\text{CO})(\text{PPh}_2\text{C}_6\text{H}_4)(\text{PPh}_3)$,¹² the orthometalated isomer of Vaska's compound, as well as of the dinitrogen Ir(I) complex *trans*- $\text{IrCl}(\text{N}_2)(\text{PPh}_3)_2$,¹³ demonstrate that flash photolysis leads in both cases to immediate appearance of a transient spectrum qualitatively the same as that attributed to " $\text{IrCl}(\text{PPh}_3)_2$ ". In the former case the transient decays by a second-order pathway (P_{CO} dependent, i.e., eq 3) to form *trans*- $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ as the photoproduct. Again it appears that the starting complex has undergone CO photodissociation to give a pentacoordinate intermediate followed by H/aryl elimination to form $\text{IrCl}(\text{PPh}_3)_2$ within the 20- μs lifetime of the flash. Thus, reductive elimination from this pentacoordinate intermediate must be at least 8 orders of magnitude faster than the rate of about $3 \times 10^{-4} \text{ s}^{-1}$ (70 °C) we have measured for the thermal reaction of $\text{H}^+\text{IrCl}(\text{CO})(\text{PPh}_2\text{C}_6\text{H}_4)(\text{PPh}_3)$ to give *trans*- $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$.¹⁴ For $\text{IrCl}(\text{N}_2)(\text{PPh}_3)_2$, photolabilization of N_2 to give $\text{IrCl}(\text{PPh}_3)_2$ is irreversible and, in the absence of the other reactants, this reactive intermediate apparently undergoes internal orthometalation of a triphenylphosphine. This is accompanied by slow absorbance decreases in the 340–550-nm range with isosbestic points at 460 and 334 nm consistent with formation of Ir(III) products. The

proton NMR spectrum of the product solutions from the continuous photolysis of $\text{IrCl}(\text{N}_2)(\text{PPh}_3)_2$ in C_6D_6 under otherwise analogous conditions displays a -2.5 ppm resonance indicating formation of an iridium hydride.¹⁵ These investigations will be described in detail in subsequent publications.

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Diagonal Peak Suppression in 2D-NOE Spectra

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The 2D correlation NMR experiments COSY¹ and NOESY² are standard techniques for study of molecular structure in solution. COSY, which is based on coherence transfer via the J coupling, has been the progenitor of a myriad of other pulse sequences for specific applications.³⁻⁵ Particularly useful have been filtered COSY pulse sequences,⁶ which are conceptually derived from multiple-quantum selective-excitation experiments.^{7,8} Double-quantum filtered COSY especially is frequently employed to suppress single-quantum peaks, improving the dynamic range and the resolution close to the diagonal.⁹ NOESY, which detects through-space magnetization-transfer via direct dipolar relaxation, frequently suffers from a more severe dynamic range problem than COSY. While use has recently been made of coherence transfer via the J coupling to selectively observe certain resonances in NOESY spectra,¹⁰ until now there has not been a general method for removing the diagonal. Thus, cross-peaks between nuclei with similar chemical shifts, which fall close to the diagonal, are obscured. Furthermore, the spectra are also often marred by strong solvent lines and t_1 noise. In this paper we describe a magneti-

(8) The following observation argues against a sequential two-photon process involving initial H_2 photolabilization to generate $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ followed by secondary photolysis of this product to give " $\text{IrCl}(\text{PPh}_3)_2$ ". The relative pulse intensity required to generate the same concentration of the latter transient was 5 times larger when the initial substrate was *trans*- $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ (under argon) than when $\text{H}_2\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ (under H_2) was the initial substrate. An alternative mechanism should be considered, namely, the possibility that both CO and H_2 are dissociated from the excited state of $\text{H}_2\text{IrCl}(\text{CO})(\text{PPh}_3)_2$. At present such a mechanism, although unprecedented, cannot be differentiated from the stepwise pathway proposed in eq 5 and 6.

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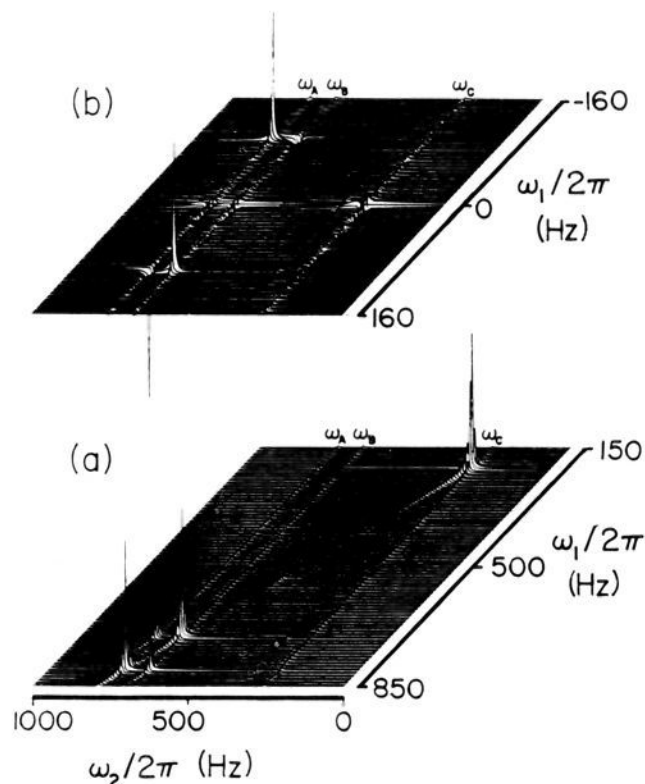
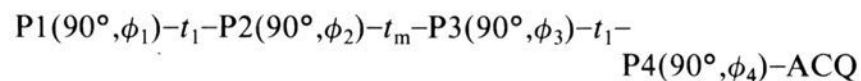


Figure 1. (a) ^1H NOESY spectrum (500 MHz, 35 °C) of a 5% solution of *N,N*-dimethylacetamide in acetonitrile- d_3 . The diagonal peaks due to the amide syn- and anti- CH_3 groups, at (ω_A, ω_A) and (ω_B, ω_B) are associated with cross-peaks at (ω_A, ω_B) and (ω_B, ω_A) arising from intramolecular chemical exchange of these residues. The cross-peak intensity amounts to approximately 30% of that of the diagonal. The signal at (ω_C, ω_C) derives from the (nonexchanging) COCH_3 group. The spectrum was acquired with sweep widths of 1 kHz in both dimensions and a t_m of 500 ms which included a 20-ms homospoil pulse. (b) ^1H spectrum of the same sample obtained with the diagonal-suppression technique. Note that the diagonal lines now appear as a horizontal row at $\omega_1 = 0$, with an intensity of about 3% of the diagonal lines in the NOESY spectrum. This spectrum was obtained under identical conditions with those used for (a), except that the sweep width in ω_1 was 2 kHz.

zation-transfer experiment which appears to offer a general solution to the dynamic-range problem in NOESY spectra and in which diagonal peaks and t_1 noise are suppressed, considerably improving spectral quality.

Our experiment consists of four pulses, a mixing (t_m) period, twin evolution (t_1) periods, and an acquisition (t_2) period as shown below:



The pulse sequence can easily be understood by first considering a thought experiment in which $\phi_4 = 180^\circ + \phi_1$, $\phi_2 = \phi_3$, and t_m is infinitesimal. During the first t_1 period the individual spins undergo forward precession. If nothing occurs during t_m , then P2 and P3 constitute a 180° refocusing pulse, so that precession during the second t_1 brings the magnetization vectors back perpendicular to ϕ_1 , resulting in no signal during acquisition. Suppose, however, that some exchange of magnetization occurs during the infinitesimal t_m . Then precession in the second t_1 will be at a different frequency from that in the first, and the magnetization will no longer echo at P4; rather, it will lie somewhere in the XY plane, and P4 will conserve the component along ϕ_4 . The signal from the cross-relaxing species will be proportional to $\sin(\omega_B - \omega_A)t_1$, where ω_B and ω_A are the precession frequencies in the second and first t_1 , respectively. Fourier transformed and phased, this gives an antisymmetric spectrum with a positive peak at $\omega_B - \omega_A$ and a negative peak at $\omega_A - \omega_B$, similar to a zero-quantum experiment.¹¹⁻¹³

For $t_m > 0$, however, this simple scheme does not work because P2 rotates the component of the complex magnetization perpendicular to ϕ_2 to $\pm Z$, leaving the other component invariant and

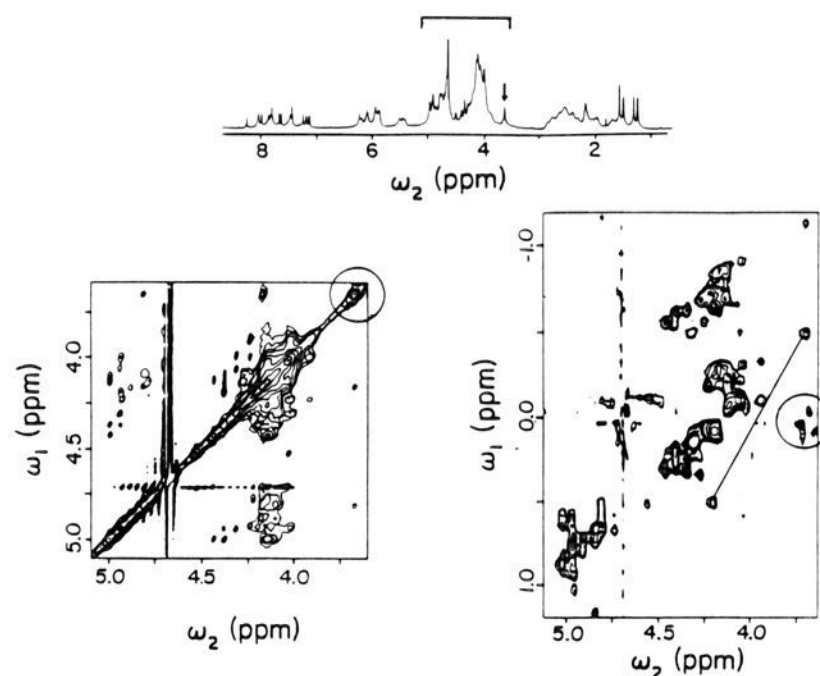


Figure 2. (Top) ^1H 1D-NMR spectrum (500 MHz, 30 °C) of the DNA dodecamer AATTbR⁵CGbR⁵CGAATT as a 1.4 mM solution in D_2O . (left) Contour plot of the 3.7–5.2 ppm region of the NOESY spectrum of the dodecamer, obtained with $t_m = 320$ ms, including a 20-ms homospoil, a recycle delay of 2 s, and sweep widths in ω_1 and ω_2 of 4 kHz. Note the strong diagonal ridge, the intense t_1 noise at $\omega_2 = 4.68$ ppm, and the crowded 4.0–4.25 ppm region. (Right) Contour plot of the same region of the 500-MHz diagonal-suppressed 2D-NOE spectrum of the same sample. Pairs of cross-peaks are connected by diagonals of slope $\Delta\omega_1/\Delta\omega_2 = 2$: this is demonstrated in the figure for the terminal 4' to 5', 5'' lines. Only positive contours are plotted. Note the lower level of t_1 noise and the absence of significant diagonal intensity. The improved resolution of our methods is best appreciated by comparing the terminal 5', 5'' proton signals (circled). Cross-relaxation peaks are resolved only in the diagonal-suppressed spectrum. Again the two 2D spectra were obtained under identical conditions except that the sweep width in ω_2 of the diagonal-suppressed spectrum was 8 kHz.

in the XY plane. The latter component dephases much faster than the former, since it is destroyed by T_2 processes as well as T_1 ; therefore, the magnetization after P3 is no longer a 180° rotation of that before P2. We can, however, preserve the real and imaginary components *separately* along Z , destroying the other with a homospoil pulse. This is done by conducting two identical experiments in which $(\phi_2)_2 = (\phi_2)_1 + 90^\circ$. If then we make $(\phi_3)_1 = (\phi_2)_1$, as before, and $(\phi_3)_2 = -(\phi_3)_1$, and add the resulting acquisitions, the *summed* magnetization after P3 will once again be a 180° rotation of that before P2. Thus, if no cross-relaxation occurs, an echo will again be formed at P4 and the non-cross-relaxing magnetization returned to Z ; while the cross-relaxing magnetization will again be modulated by $\sin(\omega_B - \omega_A)t_1$, exactly as in the thought experiment. As only the component of the magnetization parallel to ϕ_4 contains any information, the perpendicular component is discarded after the first transform, thus eliminating half the noise. This partially mitigates the loss in sensitivity over the NOESY experiment.

Figure 1 compares spectra obtained with our method and NOESY from a standard sample, *N,N*-dimethylacetamide, in which the amide methyl groups rapidly exchange with each other. In the NOESY spectrum (Figure 1a) this is revealed by cross-peaks between the two downfield proton resonances at (ω_A, ω_B) and (ω_B, ω_A) , with about 30% of the intensity of the diagonal, nonexchanged signals (ω_A, ω_A) , (ω_B, ω_B) , and (ω_C, ω_C) . In the spectrum obtained with the new technique the diagonal peaks appear at $\omega_1 = 0$ and are less than 3% of their intensity in the NOESY experiment. Methyl resonances which undergo exchange during t_m give positive peaks at $(\omega_B - \omega_A, \omega_A)$ and $(\omega_A - \omega_B, \omega_B)$, and negative ones at $(\omega_A - \omega_B, \omega_A)$ and $(\omega_B - \omega_A, \omega_B)$. The efficiency of diagonal suppression is quite apparent.

In Figure 2 we apply the pulse sequence to a more challenging system, a 1.4 mM D_2O solution of the DNA dodecamer AATTbR⁵CGbR⁵CGAATT, containing brominated cytosines, again comparing it to a NOESY spectrum taken under identical conditions. The contour plots depict the highly overlapped 3.7–5.2 ppm region, which contains the 48 3', 4', 5', and 5'' proton res-

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onances. The improved resolution of peaks close to the diagonal is apparent, as is the suppression of t_1 noise associated with the HDO signal at 4.68 ppm. Particularly impressive are the cross-peaks between the terminal 5' and 5'' protons at $\omega_2 = 3.7$ ppm. These are resolved neither in the 1D spectrum nor via NOESY. It should be pointed out that all of the cross-peaks in the region are relatively intense; where weakly coupled protons of similar chemical shift exist, the advantage of the diagonal-suppression pulse sequence over NOESY will be amplified. In a forthcoming paper¹⁴ we shall discuss in more depth the pulse sequence and its applications in both solution and the solid state.

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Synthesis and Deuteration of $(\eta\text{-Thiophene})\text{Ru}(\eta\text{-C}_5\text{H}_5)^+$: A Model for Adsorption and Deuterium Exchange of Thiophene on Hydrodesulfurization Catalysts

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While the hydrodesulfurization (HDS) of thiophene on heterogeneous catalysts has been studied extensively,² the complexity of this reaction has left most important mechanistic questions unanswered. For other heterogeneously catalyzed reactions, important mechanistic concepts have been developed by studying homogeneous reactions of model compounds.³ Few model studies of thiophene HDS have been reported.⁴ Indeed, it has not been established whether thiophene adsorbs to the surface by coordination to a metal site through the sulfur atom only⁵ or via the sulfur and the unsaturated carbon atoms (i.e., as a π -complex).⁶ Recently, Harris and Chianelli⁷ concluded, on the basis of SCF- $X\alpha$ molecular orbital calculations of metal sulfides, that the initial interaction of thiophene with second-row, catalytically active transition metals was most likely via the S atom only. They noted that the preference for S atom coordination by second-row metals was important for the higher HDS activity of these metals, in-

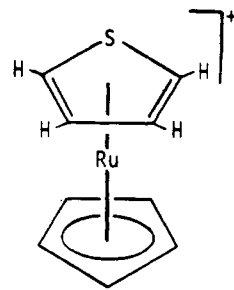


Figure 1.

cluding Ru. Supporting the conclusion that second-row metals preferred S atom coordination were the facts that there were no known π -thiophene complexes of the second- and third-row transition metals and that the only reasonably well-characterized S-bound thiophene complex was of Ru, namely, $\text{Ru}(\text{NH}_3)_5\text{-}(\text{SC}_4\text{H}_4)^{2+}$.^{8,9} In this paper, we report the first example of a π -thiophene complex, $(\eta\text{-C}_4\text{H}_4\text{S})\text{Ru}(\eta\text{-C}_5\text{H}_5)^+$ (**1**), of a second- or third-row transition metal (Figure 1). The thiophene is strongly coordinated and readily exchanges its 2,5-protons in the presence of bases or Al_2O_3 ; this latter observation suggests an explanation for the known exchange of these protons when thiophene and D_2 are passed over HDS catalysts.

The $[(\eta\text{-C}_4\text{H}_4\text{S})\text{Ru}(\eta\text{-C}_5\text{H}_5)]\text{BF}_4$ (**1**) complex was prepared by refluxing $(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}$ ¹⁰ (1.00 g, 1.38 mmol), thiophene (20 mL), AgBF_4 (0.290 g, 1.52 mmol) in 10 mL of MeOH for 72 h under N_2 . Isolation of **1** was accomplished by removing the volatiles from the reaction mixture in vacuo, extracting the residue with CH_2Cl_2 , and precipitating the product by slowly adding Et_2O . Successive recrystallizations yielded the pure air- and water-stable **1** as a pale brown powder in 60% yield.¹¹ The π -thiophene ligand is strongly bound to the Ru as shown by its slow rate of displacement (only 33% after 4.5 h) from **1** (10 mg) by $(n\text{-Bu})_3\text{P}$ (7 equiv) in acetone (0.35 mL) at room temperature.

The stability of **1** suggests that thiophene could adsorb to HDS catalysts in the π -bonded form. This form may account for the observed exchange of the 2,5-protons of thiophene when it is passed with D_2 over several catalysts (e.g., $\text{Mo}/\text{Al}_2\text{O}_3$,¹² $\text{Mo-Co}/\text{Al}_2\text{O}_3$,¹² MoS_2 ,¹³⁻¹⁵ and M_xMoS_2 ¹⁵). From ¹H NMR studies we find that the 2,5-protons of the thiophene ligand in **1** readily undergo exchange in the presence of bases. Thus, the 2,5-protons in **1** (0.003 mmol) completely exchange with deuterium (CD_3OD solvent 0.35 mL) in the presence of KOH (0.01 mmol) in less than 4 min.¹⁶ Deuteration at the 2,5-positions was established by displacing the exchanged thiophene from **1** with *tert*-butyl isocyanide and noting the almost complete disappearance of the 2,5-proton resonance of free thiophene.¹⁷ There was no evidence for exchange of the 3,4-protons. Treatment of **1** (0.017 mmol) in CD_3OD (0.35 mL) with Et_3N (0.04 mmol) resulted in approximately 50% exchange after 20 min. No exchange is observed

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